

IMPEDANCE AND MAGNETIC PROPERTIES OF STRONTIUM HEXAFERRITE NANOPARTICLES

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ABSTRACT

Magnetic nanoparticles are important physical systems, relevant for many applications, and in many cases the starting point of fundamental developments in Nanomagnetism. Strontium ferrite enjoys a high degree of chemical stability and is completely nontoxic, which makes it ideal for a wide range of applications. Magnetoplumbite-type (M-type) strontium ferrite particles have been synthesized via the sol-gel technique employing ethylene glycol as the gel precursor. The Phase, morphology and particle diameter and the magnetic properties of samples were studied by x-ray diffractometry (XRD), Scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) respectively. X-ray powder diffraction patterns showed that the samples were single-phase with the space group of P63/mmc.

The magnetic properties such as coercivity, saturation magnetization and remanent magnetization of the samples were found to be 6405.2 Oe, 28.256 and 15.2 emu/g, respectively. The thermal behaviour of the nano particles was studied using thermogravimetric analysis (TGA). The impedance analysis using complex impedance spectroscopy (CIS) technique reveals negative temperature coefficient of resistance behavior of the prepared Strontium hexaferrite nano particles.

Key words —Hexaferrite; Nanoparticle; Magnetic properties; SEM; VSM;

I. INTRODUCTION

M-type hexaferrite ($M = Ba, Sr, Pb$) crystallizes in a magnetoplumbite structure.

Hexagonal M-type $SrFe_{12}O_{19}$ plays an important role in hard magnetic materials due to their numerous applications in microwave devices, high energy recording media, magneto optic media, electric motors, magnetic components, biotechnology etc. As compared to AlNiCo magnets, sintered strontium ferrite have several distinct properties, such as relatively large saturation magnetization, superior coercivity, high uniaxial magnetic crystalline anisotropy, chemical stability, and corrosion resistivity, which stimulated researchers to tailor its magnetic properties for specific applications.

The magnetic properties and microstructural features could be improved by varying the processing parameters such as mole ratio, calcination temperature and sintering temperature, etc., Polycrystalline ferrites are supposed to be very good dielectric materials with low conductivity and have a wide technological applications in the ranges from microwave to radio wave frequencies. Moreover, $SrFe_{12}O_{19}$ are of great interest not only for their magnetic behaviour but also for the dielectric polarization inherent in their structures [1-4].

The nano $SrFe_{12}O_{19}$ structure is based on hexagonal crystal lattice with 64 ions per unit cell on 11 different symmetry sites. In this structure smaller Fe^{3+} cations are arranged over five distinct interstitial sites namely three octahedral sites (12K, 2a, 4f2), one tetrahedral (4f1) and one trigonal bipyramidal site (2b) in which five oxygen atoms surround the Fe^{3+} cation. The excellent magnetic behaviour of these ferrites can be described by the ordering of magnetic moments of the Fe^{3+} ions and the super exchange interactions between three parallel (12K, 2a, 2b) and two anti-parallel sites (4f1, 4f2) which are coupled through O^{2-} ions [5].

At higher frequency region, the magnetic nanomaterials are more useful as compared to other magnetic materials attributed to good electrical properties. The electrical and magnetic properties of $\text{SrFe}_{12}\text{O}_{19}$ are altered by various parameters such as, the method of synthesis, size and shape of the particle, chemical composition and dopants [6-10]. Ferrite systems are one of the most important eco-friendly candidates among various photo catalysts. They are being offered to yield low band gap materials which are desirable for visible light active photo catalysts.

In the present work, strontium hexaferrite powders were synthesized by sol-gel route. The structural, morphological, ac electrical and dc magnetic properties of hexaferrite powders at different calcination temperatures are studied.

II. EXPERIMENTAL PROCEDURE

The synthesis of $\text{SrFe}_{12}\text{O}_{19}$ was performed using sol-gel route. Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) was used as the solvent and gel precursor with stoichiometric weight of $\text{Sr}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (as the stoichiometric ratio of Fe/Sr is 1:4) was dissolved at a temperature of 50 °C for 2 h with continuous stirring using a magnetic stirring bar. The homogeneous solution was then placed on top of a hotplate with the magnetic stirring bar removed for dehydration to occur as this enhanced the gelation process. Slow dehydration occurred over 72–96 h at the temperature range of 100 °C and subsequently a dried gel was obtained. The dried gel, which contained finely mixed oxides of the starting materials, was then calcined at the desired temperatures for 96 h at atmospheric condition in a muffle furnace with an intermediate grinding after each 48-hour cycle of calcination, and was then quenched in air.

XRD patterns were collected using cu-K α radiation from XRD Lab-NIIST, Trivandrum and were matched using an automated XRD software package, which includes the standard JCPDS files. The Scanning electron microscopy (SEM) and FESEM micrographs was carried out for the sample calcined at 800 °C to determine the grain size and morphology of the product. The magnetic properties of the product is observed using Vibrating Sample Magnetometer at room temperature. The electrical properties were studied using complex impedance spectroscopy (CIS) technique.

II. RESULTS AND DISCUSSION

1. TG/DTA Study

Figure.1 shows TG/DTA analysis spectrum of the as synthesized sample. There is a mass loss effects in thermogravimetric curve (TG curve). The excellent hydroscopic property of the dried gel, which is relative to the big specific surface area and the porous and loose structure of the precursor nanoparticles, is confirmed by the great deal of mass loss in the temperature range of 30°C to 400°C. The mild mass loss in the temperature range of 400°C to 750°C is due to the decomposition products. And there is a no weight gain is observed in the temperature of above 800°C under nitrogen atmospheric condition which is best suited in the recent investigation [11].

The differential thermal analysis curve in Fig.1. Shows the endothermic and exothermic effects of as-synthesized sample in nitrogen atmosphere in the temperature range of 25–1000°C at a ratio of 20 °C/min. The intense endothermic effect at 70 °C shows that the free water in the dried gel may mainly occur on the gel particles and in the macro and meso pores. The weak endothermal effect at 288 °C illustrates that a little free water may be in the micro pores and capillaries. The endothermic effect at about 717 °C between two exothermic effects occurring at 650°C and 769 °C may result from the endothermal decomposition of the strontium M-type hexaferrite nanoparticles. The exothermic effects in the temperature ranges of 197 °C and 361 °C was observed.

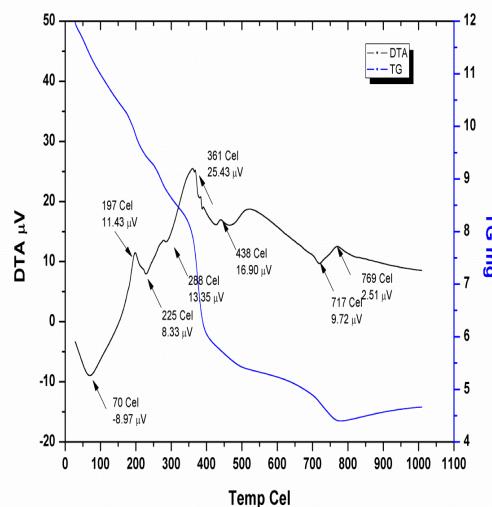


Fig.1. TG/DTA plots of as-synthesized $\text{SrFe}_{12}\text{O}_{19}$ sample

2. XRD Investigation

Figure 2 shows the XRD patterns for the three samples namely SF1, SF2 and SF3 which were calcined respectively at 600 °C, 800 °C and 1000 °C. All the reflections were indexed on the basis of the M-type structure retaining the P63/mmc space group, with the initial cell parameters of $a=5.886 \text{ \AA}$, $c=23.037 \text{ \AA}$, and the JCPDS Files (# 33-1340) had been referred to for all the peak position identification. The impurity iron oxide phase is preferentially formed at $2\theta = 31.13^\circ$ and is attributed to Fe_2O_3 (JCPDS Card #15840). In the synthesis of M-type strontium ferrite where the ratio of Sr/Fe range is 1:4, it is anticipated that substantial amount of impurity iron oxide would be formed at low calcination temperatures say 600°C and 800°C. However, at higher temperature of 1000 °C the formation of impurity iron oxide was suppressed as evidenced from the XRD pattern of the sample annealed at 1000 °C. When the calcination temperatures exceeds 800 °C, it is found that increasing the temperature improve the purity of strontium M-type hexaferrite based on the results of TG/DTA studies. Also, the intermediate grinding of these samples helps to increase the homogeneous distribution of strontium ferrite ions and the formation of final products from the precursors. The average crystallite size of the samples was deduced as 10-12 nm from the width at half height of XRD maxima by applying the Scherrer's equation.

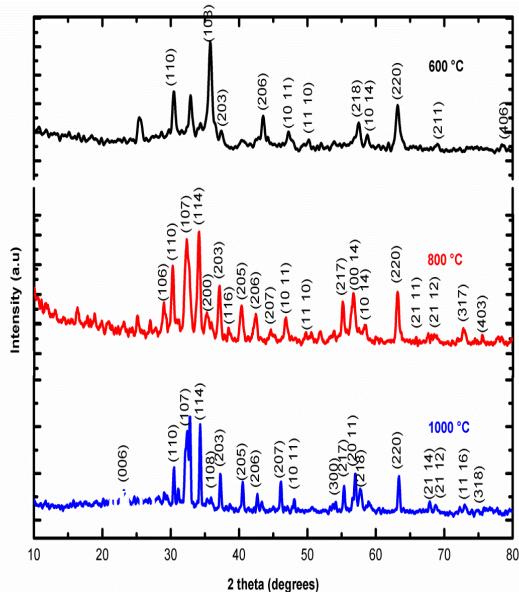


Figure 2 XRD Patterns of a series of calcinations at different temperatures of $\text{SrFe}_{12}\text{O}_{19}$

3. Morphological and Elemental Analysis

To illustrate the particle morphology during calcining treatment, the dried gel after having been heat treated at 100°C for 96 h was calcined again for 96 h at 600°C and 800 °C and then observed with HRSEM at different time duration (Figure.3). It can be seen that, all the particles are distributed homogeneously and have a proper hexagonal disc shape. When sample calcined again for at 1000 °C, it can be seen that, the particles have flake like structure. The average crystallite size calculated from HRSEM is found in the range 20 – 80 nm. HRSEM micrograph shows a cluster of strontium ferrite exhibiting faceted nature of the hexagonal ferrites. The micrograph showed clustering happened around a core center, which represented a void space created by ethylene glycol sol which was useful in modulating the distance between the ferrites. At 1000 °C, samples have coarser grains and the particles are hexagonal platelets. A well crystalline strontium ferrite nanoparticle was obtained at this temperature.

The sample calcined at 800°C mends the crystallinity of hexaferrite phase and can be described by Ostwald ripening [12]. Ostwald ripening is the process of creating large number of nanoparticles. But only a few of them can grow in size. Hence the pure and homogeneous particles of hexaferrites have been formed with hexagonal structure at 800°C (Figure 3 (c-d)).

The Energy dispersive X-ray Spectra for the samples calcined at three different temperatures are studied and confirmed the existence of $\text{SrFe}_{12}\text{O}_{19}$ at appropriate concentration without any impurities. The elemental analysis gives the presence of Sr, Fe and oxygen as constituent elements in the prepared compounds. It suggests the reasonably good distribution of elements in the material. The atomic weight percent of the constituent elements are listed in Table 3.1.

Table 3.1 The Observed Weight Percent and Atomic percent by EDX Analysis of $\text{SrFe}_{12}\text{O}_{19}$ samples at different calcination temperatures

| Sample | Elements | Observed wt. percent | Atomic percent |
|------------------|----------|----------------------|----------------|
| SF1 (600 °C) | Sr | 29.16 | 13.76 |
| | Fe | 52.67 | 38.98 |
| | O | 17.28 | 44.64 |
| SF2 (800 °C) | Sr | 23.26 | 10.68 |
| | Fe | 57.89 | 41.70 |
| | O | 18.21 | 45.80 |
| SF3 (1000 °C) | Sr | 23.96 | 09.71 |
| | Fe | 49.95 | 31.77 |
| | O | 24.34 | 54.05 |

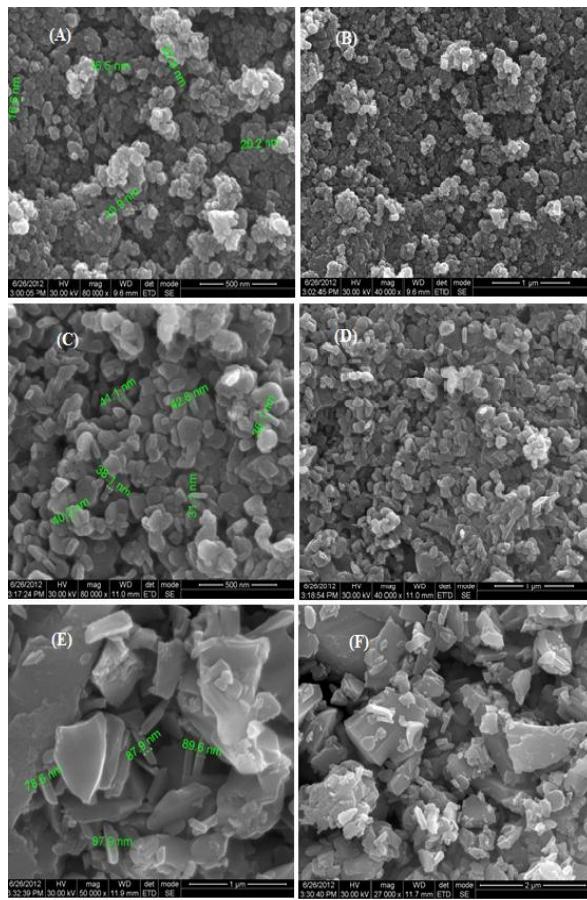


Figure 3 The High and Low magnification HRSEM Images for the samples calcined at different temperatures, (A-B) 600°C, (C-D) 800°C, (E-F) 1000°C respectively.

4. Magnetic Characteristics

a) Room temperature magnetization measurements

The sample calcined at 600°C produced a softer ferrite, which has a coercivity of 564 Oe. Annealing temperature at 800 °C produced a hard ferrite which has a coercivity of 6405 Oe and a saturation magnetization was 28.26 emu/g at the field of 19 KOe. The saturated Magnetization Ms and the Remanent Magnetization Mr at 800 °C were very closer to the theoretical value. Compared with the values reported in literatures, the coercivity, saturation magnetization and remanent magnetization was well improved when the ratio of Sr/Fe was $\frac{1}{4}$ at 800 °C. (Table 3.2 and Figure 4). The small value in saturation magnetization M_s is attributed to the surface spin disorder of hexaferrite nanoparticles. The increase of calcination temperature by 200 °C increases the coercivity by 91% and reduced the saturation and remanent magnetizations. Also, at the calcination temperature 1000 °C, the sample has a coercivity of 5282 Oe was observed. There is no significant change was detected by increasing the temperature to 1000 °C.

Table 3.2 Tabulated results for VSM measurements for the samples at different annealing temperatures

| Ferrites | Temperature (°C) | Hc (Oe) | Ms (emu/g) | Mr (emu/g) | Squareness ratio (SQR) |
|----------|------------------|---------|------------|------------|------------------------|
| SF1 | 600 | 563.85 | 39.59 | 16.4 | 0.41 |
| SF2 | 800 | 6405 | 28.26 | 15.2 | 0.54 |
| SF3 | 1000 | 5282 | 22.96 | 13.2 | 0.57 |

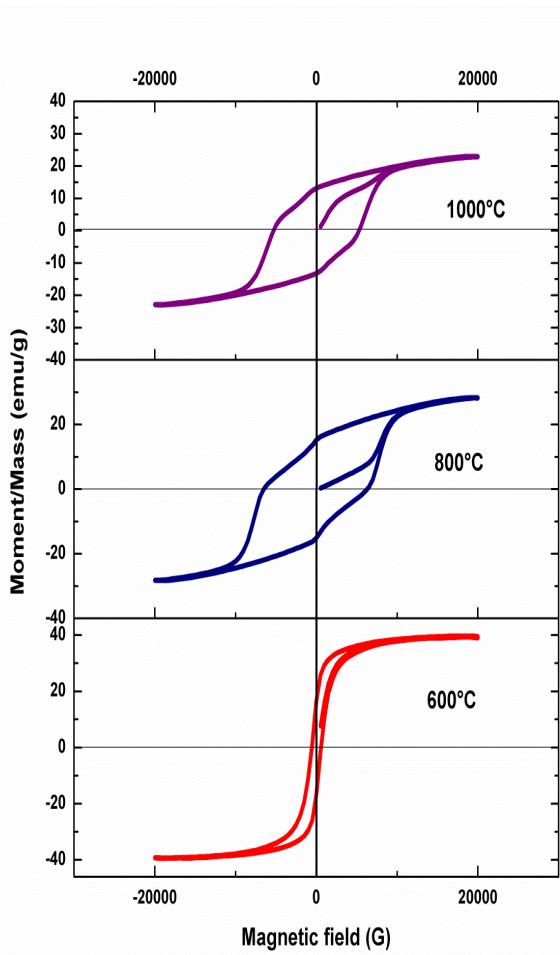


Figure 4 Hysteresis curves at different annealing temperatures using VSM

It is seen from the figure that the saturation magnetization M_s decreases as the calcination temperature is increased from 600 °C to 800 °C. This may be due to the formation of non-magnetic phase, Fe_2O_3 , as can be seen from XRD (Figure 2). There is no significant reduction in M_s at 1000 °C was observed. It is known that the energy of a magnetic particle in an external field is proportional to its size via the number of magnetic molecules in a single magnetic domain. When this energy becomes comparable to thermal energy, thermal fluctuations will significantly reduce the total magnetic moment in a given field [13].

Samples at 800 °C and 1000 °C did not show any significant difference in the value of squareness ratio ($SQR = M_r/M_s$). The Squareness ratio is essentially a measure of how square the hysteresis

loop and is given by the ratio of M_r/M_s . The relative high value of $SQR (> 0.25)$ suggested that the three samples may be multi-domains in nature [14]. In general, large SQR values are desired for recording medium. It is observed that coercivity was increased in the magnetic nanostructures at higher calcination temperatures. This may be due to the existence of exchange bias which causes a shift of hysteresis loop when in field cooling. This exchange bias phenomenon observed could be due defect-induced exchange bias by the existence of oxygen-vacancies in the M-type structure.

b) Temperature Dependence of Magnetization Measurements

The temperature dependence of the magnetization curve for the sample annealed at 800 °C as a function of the magnetic field intensity is illustrated in the Figure 5. It is observed that, the magnetic susceptibility decreases initially with increasing temperature, then increases and decreased drastically at the region of Curie temperature at 828 K. Such behaviour suggests the existence of the nano magnetic material in single domain. Thermodynamically, the formation of a domain wall is not possible when $KV \gg kT_0$. Where K is magnetic anisotropy constant, V is the particle volume and kT_0 is Boltzmann energy term [15]. Since the large magneto crystalline anisotropy in hexaferrite is due to the unique axis of magnetization, that is along c-axis, Hopkinson effect could be favoured in single domain particles of strontium hexaferrites [16-17]. The Curie temperature of strontium is found experimentally as 828 K and it depends on the grain size, magneto crystalline anisotropy and saturation magnetization.

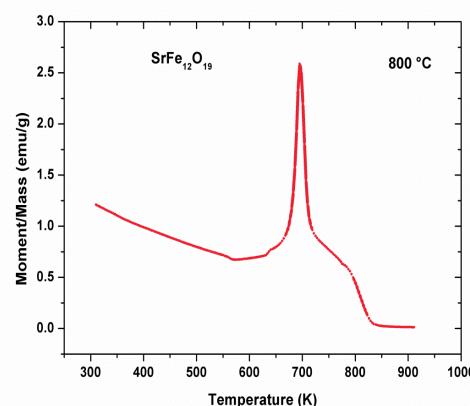
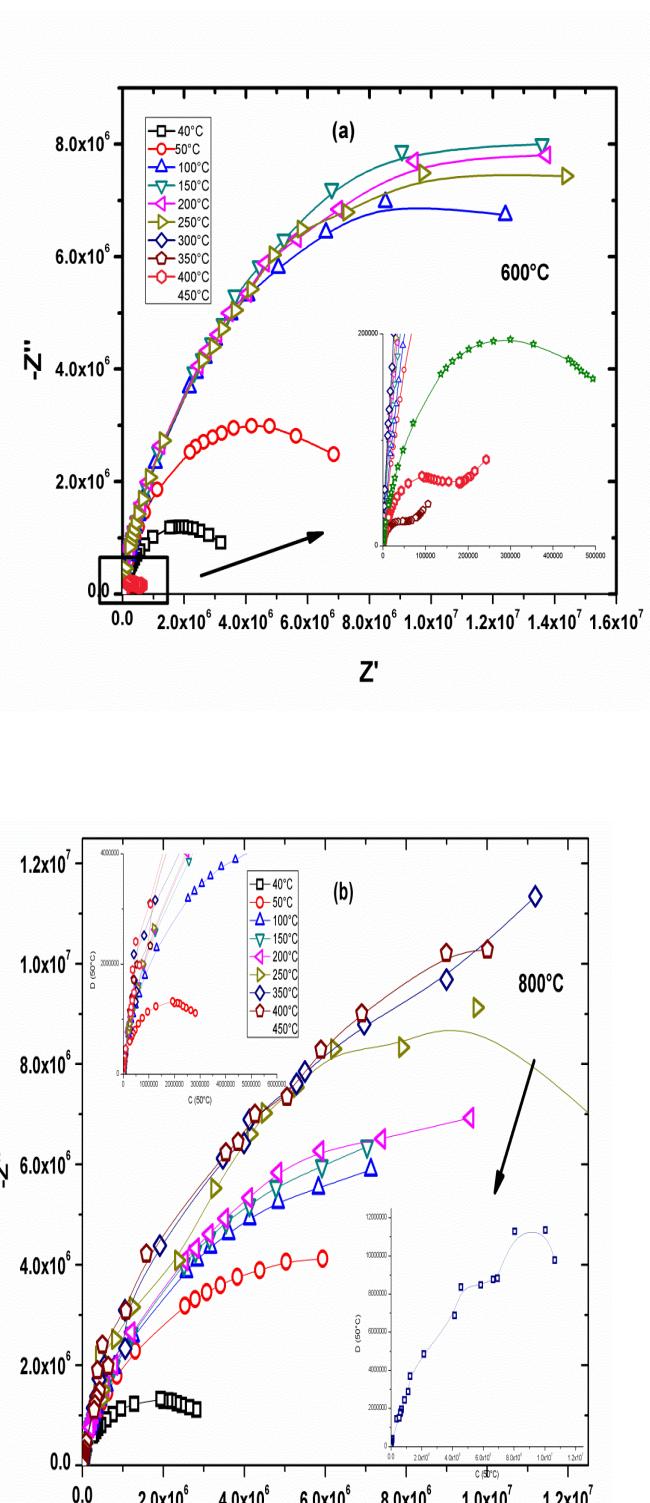


Figure 5 M-T curve for the Strontium hexaferrite calcined at 800 °C

5. Impedance Analysis

The electrical properties of $\text{SrFe}_{12}\text{O}_{19}$ material were investigated by complex impedance spectroscopy (CIS) technique. Figure 6 (a-c) shows the temperature dependent Nyquist plot of $\text{SrFe}_{12}\text{O}_{19}$ material calcined at three different temperatures. The impedance spectra are characterized by the appearance of a single semi-circular arc. For the sample calcined at 600°C , the single semicircular arc is observed. Whereas at high calcination temperatures like 800°C and 1000°C two semi-circular arcs at specific temperatures are observed. The single semi-circular arc suggests the presence of grain interior property of the material. It has been observed that the bulk resistance of the material decreases with increase in temperature from room temperature to 300°C showing a typical semiconducting property, i.e., negative temperature co-efficient of resistance behaviour. The intercept of the semi-circular arc with the real axis (Z') gives us an estimate of the bulk resistance (R_b) of the material. Thus, the bulk of grain effects strongly dominates the conduction of the strontium hexaferrite at all the temperatures.

A new semi-circular arc in the Nyquist plots of the impedance at 1000°C is an indication of another type of conduction process. The presence of two semi-circular arcs is observed above 300°C clearly is due to the contribution from grain boundary. The arc on lower frequency regime is due to the grain boundary conduction and that on the higher frequency side is due to the grain conduction. With increasing calcination temperatures, the diameter of the semi-circular arc related to grain boundary expands while that of the bulk of the grain depresses.



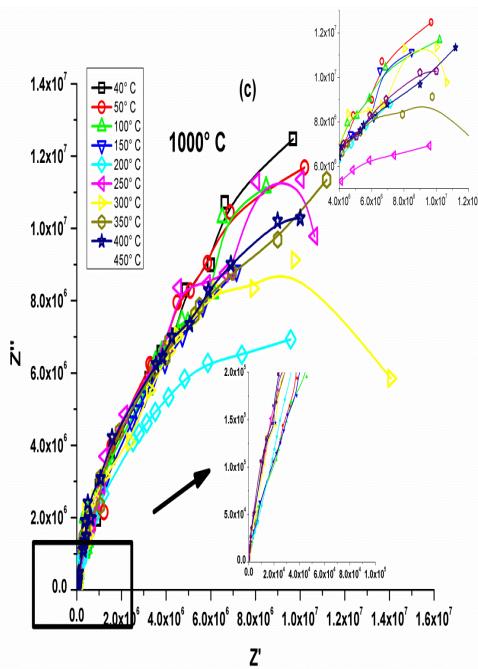


Figure 6 (a-c)Impedance spectra of samples SrFe₁₂O₁₉ for different calcination temperatures (A) 600°C (B) 800°C (C) 1000° C.

IV CONCLUSIONS

Single phase single domain M-type strontium hexaferrite SrFe₁₂O₁₉ nano particles with nominal composition were prepared by sol-gel route calcined at 800 °C. Magnetic measurements exhibit hard ferromagnetic hysteresis behaviour. The VSM result reveals that the ultrafine strontium hexaferrite nanoparticles with optimum magnetic properties can be obtained when calcined at 800 °C. Initial magnetization curve and the Squareness ratio confirm the single domain structure. Temperature dependent magnetization measurements also confirm the single magnetic domain nature due to the occurrence of Hopkinson peak. Impedance analysis at temperature reveals a normal semiconducting behaviour. From the dielectric measurement results, it has been found that non-Debye type of relaxation prevails in the prepared nano samples. This method of preparation (calcinations at 800°C) creates oxygen vacancies at higher calcination temperatures which contribute the conduction process. Due to the existence of oxygen vacancies the dielectric loss is also high at high temperatures.

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